

## Application of Fluorescence Microscopy to Coal-Derived Resid Characterization

R.F. Rathbone, J.C. Hower and F.J. Derbyshire

Center For Applied Energy Research, Lexington, Kentucky 40511-8433

Keywords: Microscopy, Fluorescence, Resid

### INTRODUCTION

This study evaluates the usefulness of a fluorescence microscopy methodology to analyze coal-derived resids and interpret the data in the light of liquefaction processing conditions, process response, the inferred resid reactivity, and in relation to results of other analytical data. The fluorescence technique utilized has been widely applied to coal and kerogen characterization, albeit with some modifications, but is novel in its application to the characterization of coal liquids.

Fluorescence is the emission of light energy which occurs when electrons, having been excited to a higher energy orbital, return to their lower energy ground state. The majority of organic molecules that fluoresce are those with conjugated double bonds (chromophores), such as aromatics, characterized by pi-electrons less strongly bound within the molecule than sigma electrons, that can be excited to anti-bonding pi-orbitals (1,2,3). Increasing the extent of pi-bond conjugation (i.e. larger molecular size) generally imparts a shift in absorption and emission spectra to longer wavelengths. Resid fluorescence largely depends on the concentration and degree of conjugation of aromatic chromophores in the high molecular weight liquids, possibly with ancillary effects from oxygen functionalities. In this context, fluorescence analysis of liquefaction resids can potentially evaluate process performance, since direct liquefaction processes endeavor to break down the macromolecular structure of coal, and reduce the molecular weight of polycondensed aromatics through hydrogenation, the opening of ring structures, and heteroatom removal.

### EXPERIMENTAL

Composited Wilsonville CC-ITSL resid samples (combined samples from an entire liquefaction run) received from Consolidation Coal Co., Pittsburgh, PA, consisted of eight non-distillable (at 850°F\* or 454°C\*) coal liquids (resid) from runs 251-II, 259, 250, and 257. In addition, four pressure filter liquids (PFL) were supplied from the HRI ITSL bench unit, Run I-27 (Table 1). The Wilsonville resids are designated as "interstage" (sampled between the first and second reactor stages) and "recycle" (sampled after the second reactor stage). Samples from HRI Run I-27 are designated with a number representing the sampling day (e.g. PFL P2 = run day 2). Each resid sample was added to several drops of cold setting epoxy resin (with hardener), placed into an epoxy pellet cavity, and allowed to harden. After setting, the sample surface was ground and polished by hand on a rotating lap using a series of grinding papers and alumina polishing compounds.

Fluorescence emission from the resids' polished surface was measured with a Leitz MPV Compact microscope photometer, equipped with a diffraction grating monochromator, a photomultiplier tube, and a 100 W mercury arc lamp (as an excitation source). A Leitz Ploemopak vertical illuminator, housed the necessary filters for ultraviolet-violet (355 to 425nm) illumination, and supported a 50X air immersion objective in the light path. The microscope photometer was interfaced with a computer for data acquisition. Fluorescence spectra were acquired, in argon gas to inhibit photo-oxidation during the analyses, by recording fluorescence intensities every 2.5nm (nominal resolution of 5nm) from 470nm to 700nm. The fluorescence emission from a selected area of resid was scanned 20 times and averaged to get one spectrum per resid particle. Raw spectral data were normalized, a correction factor applied, and then re-normalized so the maximum intensity equaled 100%. The

uncorrected spectra were used to assess fluorescence intensity differences between samples by calculation of the area beneath the spectra. Unlike other chemical analysis methods employed to characterize the liquefaction resids (e.g. refs. 4 & 5), the precision was difficult to evaluate due to inherent variabilities within the Wilsonville resid samples. However, results from replicate fluorescence analyses on the optically homogeneous pressure filter liquids from HRI Run I-27 indicated that fluorescence spectra are repeatable within 3 to 4 nm.

The random reflectance at 546nm off a polished resid surface was obtained utilizing the same microscope photometer employed for fluorescence analysis. A 100 W tungsten-halogen lamp was the illuminant, and isotropic glass standards were used for system calibration. Reflectance analyses were conducted in air immersion because of observed interactions between the resids and microscope immersion oil.

### III. Results and Discussion

#### A. Interstage vs. Recycle Resids

**Run 251-II (Wyodak coal, T/C)** Fluorescence spectra from the Run 251-II interstage and recycle resid samples are shown in figure 1a, and reveal a shift of the recycle resid fluorescence spectra to shorter wavelengths (spectral "blue shift") compared to the interstage resid. A small, discrete portion of the recycle resid, not shown, displayed a relatively intense yellow fluorescence with an wavelength of maximum intensity ( $L_{max}$ ) of 578 nm. It is possible that it represents one of the three pasting solvent components from the V131B solvent surge tank that was incompatible with the other two components. The mean random reflectance of resids from Run 251-II decreased slightly from the interstage to recycle sample, and, analogous to vitrinite reflectance (6), is considered to represent a decrease in the degree of aromatization and condensation of the recycle resid.

**Run 250 (Illinois #6 coal, T/C)** A fluorescence spectral "blue shift" and fluorescence intensity increase was recorded for the Run 250 recycle resid compared to its interstage equivalent (Figure 1c). Mean reflectances of the resids decreased by 0.54% from the interstage to recycle sample (Table 1). The difference is significant, as it is greater than 3 standard deviations from the mean values of each sample.

**Run 257 (Illinois #6 coal, C/C)** Qualitative observations of resid fluorescence revealed substantial variations in these samples, represented quantitatively in figure 1d as two general fluorescence "populations". The origin of this fluorescence variability is not yet known. However, figure 1d does show that, like the Run 251-II and Run 250 resids, the recycle resid fluorescence spectra are at shorter wavelengths than the interstage spectra. The mean resid reflectances from Run 257 decreased by 0.34% from interstage to recycle.

Accompanying the fluorescence "blue shift" of the recycle resids compared to their interstage equivalents, is a decrease in the percentage of aromatic protons, an increase in beta+gamma (= aliphatic) protons, and a shift of the phenol peak location to higher wavenumbers (smaller aromatic ring size) in the recycle sample (Table 1). The fluorescence and chemical data from the Run 251-II and 250 resids suggest that the catalytic second stage provided considerable upgrading of resid produced in the thermal liquefaction unit (TLU). This is not unexpected since it is generally considered that the primary role of the first stage TLU is to dissolve the coal (and recycled resid), whereas the second stage upgrades the first stage products (7). Resid from the first stage is derived from the recycle solvent and coal that has been processed for the first time, whereas resid sampled after the second stage catalytic reactor is mainly derived from coal liquids and a much smaller proportion of unreacted coal. It is therefore plausible that the catalytically hydrogenated recycle resid sample displayed a more intense fluorescence, at shorter wavelengths than the interstage sample, indicating the presence of less condensed, lower molecular weight aromatic structures. A similar interpretation is suggested for the Run 257

(catalytic/catalytic) resids: the catalytic second stage has upgraded the products from the catalytic first stage, consistent with the suggestion that some aromatics from the first stage reactor resid product were hydrogenated to less condensed structures.

The selective rejection of preasphaltenes in the critical solvent deasher (CSD) might also have effected the observed fluorescence properties of the Wilsonville resids. A preferential removal of condensed, high molecular weight aromatics can occur in this processing stage, and would contribute to a fluorescence intensity increase and spectral blue shift of the recycle resid.

**Run 259 (Pittsburgh coal, C/C)** Similarities in the average fluorescence spectra (Figure 1b) and intensities of the interstage and recycle samples suggest that the second catalytic stage in Run 259 did not substantially alter the overall molecular size or concentration of aromatics after the resid had been through a catalytic first stage. The recycle resid exhibited a reflectance slightly lower than that of the interstage sample, although the reflectance values were nearly within one standard deviation of each sample. The minor changes in fluorescence and reflectance properties between the interstage and recycle samples correspond to other chemical properties. The data revealed only a slight decrease of aromatic protons in the recycle sample, and a small increase in beta+gamma proton content.

## **B. Comparisons Between Wilsonville Runs**

The comparisons of the interstage and recycle resid fluorescence properties suggest the spectral distribution and intensity are potential indicators of liquefaction process performance. Strongly bonded high molecular weight condensed aromatic structures, that are likely to be more refractory to upgrading than lower molecular weight less condensed aromatic compounds, would exhibit fluorescence with a low intensity, at comparatively long wavelengths. Conversely, intensely fluorescing resids with spectral distributions at shorter wavelengths are inferred to be relatively reactive to further upgrading.

**Interstage Resids** The fluorescence spectra of the interstage resids (Figure 2a) suggest the products from Run 259 (Pittsburgh coal, C/C) and Run 251-II (Wyodak coal, T/C) are the least reactive, with relatively low fluorescence intensities, and fluorescence peaks at 700nm or greater. The Run 259 resid is assumed to be comprised of larger, more condensed aromatic structural units than the resid produced in Run 251-II, as indicated by a low fluorescence emission in the 470nm to approximately 600nm region. Proton NMR data indicate the interstage resid from Run 259 has approximately the same percentage of total aromatics as the Run 251-II counterpart, although the latter has relatively more uncondensed aromatics than Run 259 resid. This is not unexpected considering the differences between the two feedstocks: product derived from the subbituminous Wyodak coal is expected to contain smaller, less condensed aromatic structural units than the bituminous-rank Pittsburgh coal. The Run 250 (Illinois #6 coal, T/C) interstage resid has a fluorescence spectrum that is shifted to shorter wavelengths than that of the Run 251-II (Wyodak coal, T/C) or Run 259 (Pittsburgh coal C/C), with an average intensity that is slightly greater than or equal to Run 251-II, but significantly lower than the Run 259 resid. Relative to Run 259, interstage resid from Run 250 was slightly more aromatic (from NMR data in Table 1), contributing to a fluorescence intensity reduction. However, it contains relatively fewer condensed aromatics and more uncondensed aromatics than the interstage resid from Run 259 (hvAb feedstock), probably causing the observed spectral "blue-shift" of the Run 250 resid.

Despite the variability in fluorescence properties of the Run 257 (Illinois #6 coal, C/C) interstage resid (Figure 2a), it is evident that the fluorescence emission of this product is substantially shifted to shorter wavelengths

relative to the other Wilsonville interstage samples investigated. In addition, the total interstage resid composite was substantially less aromatic than the other Wilsonville interstage resids (>10% difference in aromatic protons), with evidence of overall smaller aromatics (phenol peak shifted to higher wavenumbers). The reflectance percent was also significantly lower than the other Wilsonville resids (Table 1), probably due to the lower aromatic content and reduced condensation of the aromatic molecules.

**Recycle Resids** Between the runs, similar relationships hold for the fluorescence properties of the recycle resids as for their interstage equivalents, figure 2b. As shown in the figure, the average fluorescence spectrum from the Run 251-II (Wyodak coal, T/C) recycle resid was somewhat similar to that from Run 250 (Illinois #6 coal, T/C). Compared to the other Wilsonville resids studied, the Run 257 recycle resid contained the lowest concentration of aromatic protons, while it also had the highest percentage of beta+gamma protons and the phenol peak at a higher wavenumber ( $3302\text{ cm}^{-1}$ ) (Table 1).

### C. HRI Run I-27 Resids

The wavelength of maximum intensity ( $\lambda_{\text{max}}$ ) of the Run I-27 resids was substantially shifted to longer wavelengths from sample PFL P2 to PFL P18 (Figure 3a), along with a monotonic reduction in relative intensity at the shorter wavelengths, indicating aromatic ring condensation increased as the run progressed. Figure 3b indicates that sample PFL P2 had the greatest average fluorescence intensity, whereas sample PFL P25 had the lowest intensity, suggesting an increased concentration of aromatic chromophores (causing an increase in energy delocalisation) occurred over the course of the run. There was also a progressive increase of resid reflectance from sample PFL P2 to P25. The trends exhibited by the fluorescence and reflectance properties are accompanied by systematic chemical changes. From sample PFL P2 to P25, there is a monotonic increase in percent aromatics, a decrease in beta+gamma proton concentrations, and a shift in phenol peak frequency from  $3305$  to  $3296\text{ cm}^{-1}$  (Table 1), indicative of increasing ring condensation.

The fluorescence "red-shift", intensity decrease, and increase in resid reflectance percent over the course of Run I-27 suggest that, with an increase in age, the catalyst became less effective in upgrading the non-distillable fraction of coal liquids to low molecular weight, less aromatic products as aromatic ring hydrogenation became less pronounced during the run. A possible cause of these deleterious changes in resid properties over the course of the run is the partial deactivation of catalyst from deposition of carbonaceous materials onto the catalyst surface, which is believed to occur most rapidly in the early stages of the liquefaction run (8). Other process variables that may have influenced resid fluorescence and chemical properties include increased reactor temperatures, a solvent/coal ratio reduction, and an increase in the solvent cut-point (9).

## VI. Summary and Conclusions

Quantitative fluorescence microscopy is potentially a rapid, inexpensive technique which can provide new insight into the structure and composition of coal-derived resid, and could lead to more effective process control. Perhaps the greatest strength of quantitative fluorescence microscopy is its ability to resolve inhomogeneities within coal-derived resid samples, including, but not limited to, minerals, unreacted macerals, and multiple resid phases. This capability is not possible with most other analytical techniques which typically require resid dissolution in a solvent prior to analysis. Whereas these analytical techniques provide chemical and structural information on a homogenized resid sample, and only on the soluble portion, inherent variability within the coal liquids can be identified and measured with fluorescence microscopical methods.

### Acknowledgements

This work was supported by subcontract from Consolidation Coal Co. under U.S. Department of Energy Contract No. DE-AC22-89PC89883.

### VII. References

- (1) Bridges, J.W., In *Luminescence in Chemistry* (Ed. E.J. Bowen), D. Van Nostrand Co., 1968, pp. 77-115.
- (2) Wehry, E.L., In *Fluorescence: Theory, Instrumentation and Practice* (Ed. G.G. Guilbault), Marcel Dekker, 1967, pp. 37-132.
- (3) George, G., In *Luminescence Techniques in Solid State Polymer Research* (Ed. L. Zlatkevich), Marcel Dekker, 1989, 318 pp.
- (4) Robbins, G.A., Winschel, R.A. and Burke, F.P., *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 1985, 30(4), pp. 155-163.
- (5) Winschel, R.A., Robbins, G.A. and Burke, F.P., *Fuel*, 1986, 65, pp. 526-532.
- (6) McCartney J.T. and Teichmuller, M., *Fuel*, 1972, 51, pp. 64-68.
- (7) Derbyshire, F.J., Varghese, P. and Whitehurst, D.D., *Fuel*, 1983, 62, pp. 491-497.
- (8) Derbyshire, F.J., *Catalysis in Coal Liquefaction: New Directions for Research*, IEA Coal Research, 1988, 69 pp.
- (9) Consolidation Coal Co., personal communication to authors.

Table 1

Run No.	Coal	Sample <sup>1</sup> Type	Proton NMR Data <sup>2</sup>		Peak <sup>3</sup> (cm <sup>-1</sup> )	Reflectance <sup>4</sup>	
			Arom. (%)	Bet+Gam (%)		(%)	s.d.
251-II	Wyodak	T/C, Int	33.2	37.6	3294	7.80	0.22
251-II	Wyodak	T/C, Rec	26.8	44.8	3298	7.66	0.25
259	Pittsburgh	C/C, Int	33.3	35.6	-	7.82	0.11
259	Pittsburgh	C/C, Rec	31.5	40.2	-	7.70	0.26
250	Illinois #6	T/C, Int	34.5	35.3	3292	7.84	0.13
250	Illinois #6	T/C, Rec	26.1	45.2	3299	7.30	0.15
257	Illinois #6	C/C, Int	21.8	49.5	3300	6.82	0.20
257	Illinois #6	C/C, Rec	19.9	52.0	3302	6.48	0.19
I-27	Illinois #6	C/C, Day 2	14.5	57.3	3305	6.21	0.12
I-27	Illinois #6	C/C, Day 8	20.7	51.0	3301	6.80	0.07
I-27	Illinois #6	C/C, Day 18	29.2	40.5	3297	7.57	0.14
I-27	Illinois #6	C/C, Day 25	38.3	32.8	3296	8.06	0.08

1. T/C = thermal/catalytic, C/C = catalytic/catalytic, Int = interstage resid, Rec = recycle resid
2. Arom. = aromatic protons, Bet+Gam = beta and gamma protons (ref. 5)
3. Peak = FTIR phenol peak location (see ref. 4)
4. (%) = mean reflectance %, s.d. = standard deviation

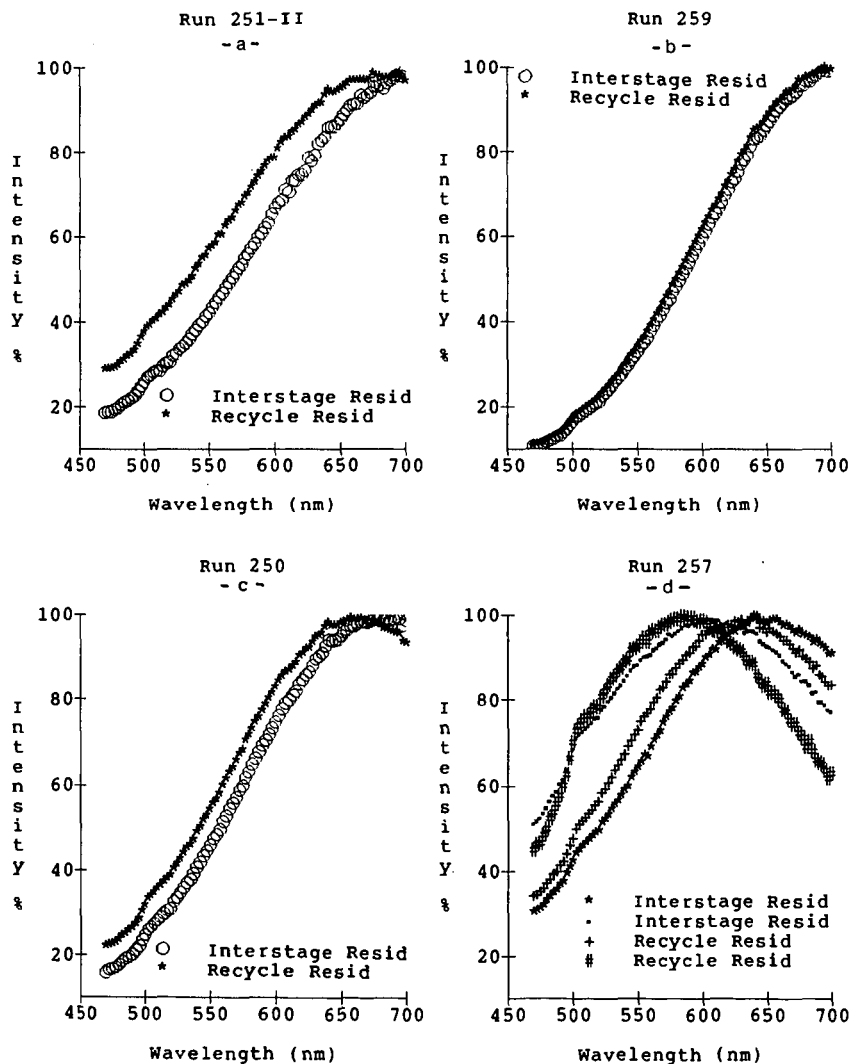


Figure 1. Corrected fluorescence spectra of resids from Run 251-II (a), Run 259 (b), Run 250 (c), and Run 257 (d). Data for each resid sample represent the average of five spectra.

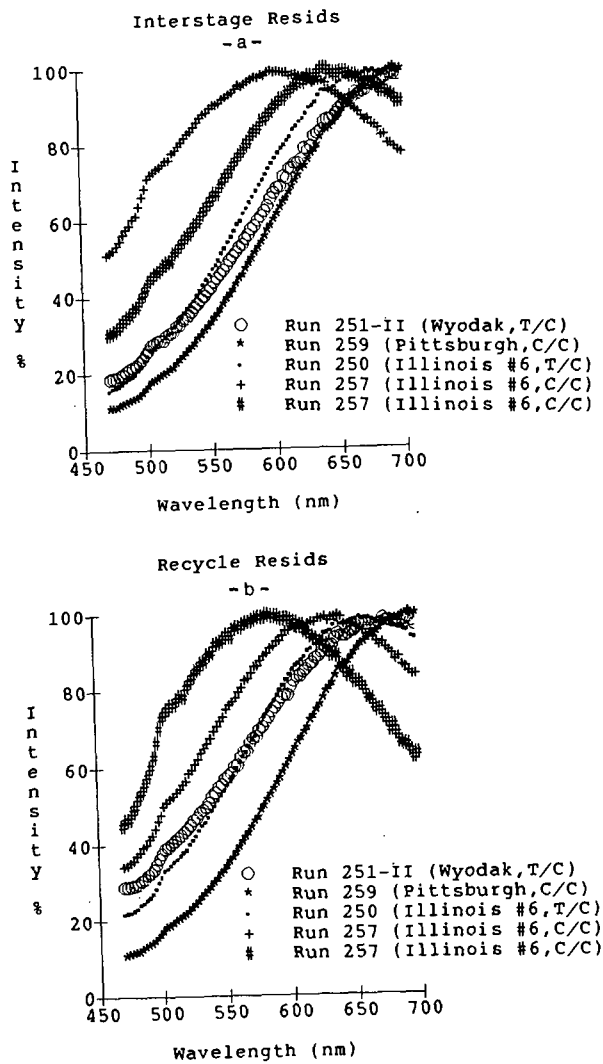


Figure 2. Corrected fluorescence spectra for the Wilsonville interstage (a) and recycle (b) resids. Data for each resid sample represent the average of five spectra.

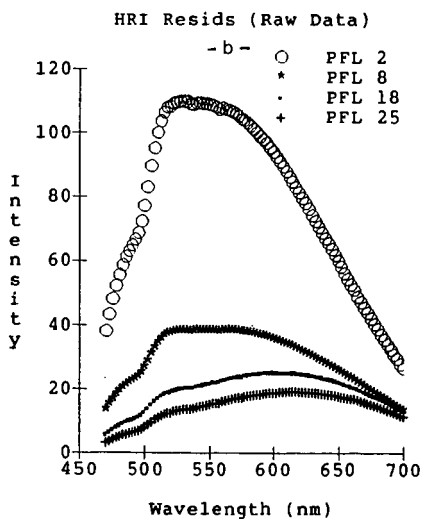
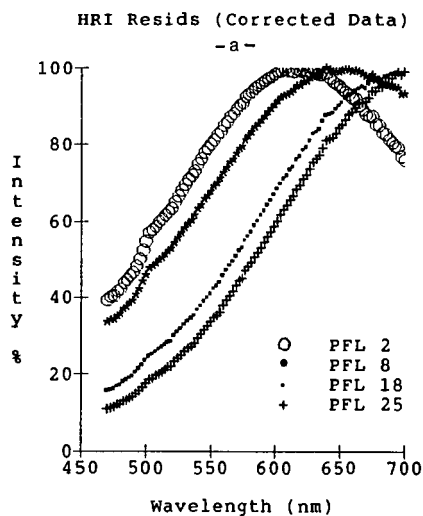


Figure 3. Corrected (a) and uncorrected (b) fluorescence spectra for HRI Run I-27 PFL resids. Data for each resid sample represent the average of five spectra.